

# PATENT SPECIFICATION

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## (54) PROCESS FOR TREATING WASTE OIL

(71) I, LIONEL BORENSTEIN, a Canadian citizen of 1470 Beverly Crescent, Chomedey, P.Q. Canada, do hereby declare the invention, for which I pray that a patent may be granted to me and the method by which it is to be performed to be particularly described in and by the following statement:

- 5 The present invention relates to an improved process for purifying, refining or reconditioning used lubricating oils. 5
- 10 In recent years, two problems have become increasingly important with regard to lubricating oils. The first is one of increased scarcity of petroleum with the resulting higher cost of petroleum products. This problem is one that is shared with minerals and other non-renewable natural resources and reflects on lubricating oils as most lubricating oils are of petroleum origin. The second relates to pollution of the environment associated with the disposal of used lubricating oil or some of the by-products of current re-refining process. Most used lubricating oil contains relatively high quantities of lead and other metallic contaminants, so that it cannot simply be dumped or burned as fuel without seriously polluting the environment. The use of this material as fuel would also increase burner maintenance costs due to the high level of contaminants present. 15
- 20 Changes in the formulation of lubricating oil in recent years have created problems with regard to re-refining. The need for longer intervals between oil changes, higher oil pan temperatures and reduced oil capacities of engines have caused the use of a wide range of more sophisticated additives in order to meet the more exacting operating conditions. Unfortunately, the increased effectiveness of the additives in the oil results in increased difficulty in removing them in the re-refining process. 20
- 25 Most used lubricating oil refiners use sulfuric acid in their process and are faced with the environmental problems in disposing of the acid by-products. 25
- 30 In a typical re-refining process, waste lubricating oil as collected from automotive service stations, or used railway diesel lubricating oil, is subjected to a preliminary predistillation step by heating to about 550 - 600°F. This distills off the light boilers (water, gasoline, solvents, some unsaturated hydrocarbons, etc.) and thermally degrades some of the additives in the oil. The resulting stripped oil is then acid treated by mixing with about 5% of concentrated sulfuric acid by volume. This step produces a noxious acid sludge of about 16% by volume of the initial stripped oil. This material is allowed to settle in a cone-bottomed vessel, drawn off and usually trucked away to land fill sites. The acid sludge contains metals and other impurities from the used oil. The decanted oil from the acid contactor is mixed with clay, heated to 500 - 600°F. and treated with superheated steam over a period of about 15 hours. This clay-steam treatment removes unstable compounds and gives the oil its desired colour and odour. The oil-clay mixture is then passed through a filter (usually a plate and frame press) yielding a base stock lubricating oil. Equipment corrosion problems are common in the clay treating step, due to residual acid in the oil. 35
- 40 The acid treatment is very effective in removing metallic contaminants from the oil. It is also effective in removing organic contaminants such as oxidation products and resins that form in the oil. These organic contaminants contribute to filtration problems (blinding of paper, etc.) and if not removed can contribute to fouling of equipment in other treatments such as vacuum distillation or hydrotreating when such treatments are used as part of a re-refining operation. 40
- 45 Some new proposed processes, while effective in reducing metallic contaminants in used 45

lubricating oil, do not appreciably reduce organic contaminants.

An undesirable feature of other suggested processes is that larger proportions of solvents are used in relation to the amount of oil being treated. These solvents have to be reclaimed, with some unavoidable loss and at some expense.

5 According to the present invention, there is provided an economical process which is effective in reducing both metallic and organic contaminants of used lubricating oil without the necessity of costly reclamation of solvents, since relatively low levels of ingredients are used which can be considered consumed in the process.

10 The novel process of the present invention comprises mixing a used lubricating oil with an aqueous solution of a water soluble oxidizing agent capable of supplying active or nascent oxygen and a coupling agent having mutual affinity for both water and the used oil thereby causing the precipitation of a sludge containing the impurities, separating the sludge and recovering the purified oil.

15 More specifically, the process of the present invention comprises treating used lubricating oil with a coupling agent and an aqueous solution of an oxidizing agent, thereby to inactivate those components in the oil which are responsible for the suspension of impurities and thus causing the impurities to precipitate.

20 Either before treatment of the used lubricating oil with the aqueous solution of oxidizing agent or at the same time there must be used a coupling agent in order to effectively inactivate those oil components such as dispersants, detergents and emulsifiers which are incorporated in the oil to suspend the metallic and organic impurities which develop in the normal usage of lubricating oil. The coupling agent is a material which has a mutual affinity for the oil components responsible for the separation of impurities and water.

25 As far as the used lubricating oils which can be treated in accordance with the present invention there may be mentioned oils used for lubricating automotive, railway and marine engines or equipment, farm or industrial vehicles or equipment and other industrial lubricating oils such as those used for metal working, cutting and machining of metals. Such oils generally contain some additives such as, for example, dispersants, detergents, emulsifiers, corrosion inhibitors, oxidation inhibitors, viscosity index improvers, pour point depressants, antiwear or extreme pressure additives and antifoams.

30 The oxidizing agent used in accordance with the present invention is a compound which is capable of supplying active or nascent oxygen. As examples of such components, there may be mentioned ammonium, sodium or potassium persulfate, potassium monopersulfate, hydrogen peroxide, sodium hypochlorite, sodium dichromate and succinic acid peroxide, though ammonium persulfate is preferred. The essential requirement for the oxidizing agent is that it be water soluble and that its active oxygen be readily available to inactivate the appropriate components present in the used lubricating oil. The level of the oxidizing agent used can vary between the range of from about 0.1 to about 10% by weight of the used oil being treated. In practice, the oxidizing agent is preferably used at a level of 0.1 to 3% by weight for economic reasons.

40 The coupling agent used in accordance with the present invention is a compound which is a mutual solvent or has a mutual affinity for both water and the used oil. The coupling agent improves the water miscibility of the oil and thus enables the oxidizing agent to effectively act on the impurity suspending components in the used lubricating oil.

45 The unexpected results of the process of the present invention are believed to be due essentially to the fact that the coupling agent favors the breakdown of the impurity suspending components of the oil by favoring their oxidation by the oxidizing agent thereby permitting precipitation of the undesired impurities which may during the process be also partially oxidized. In the prior art, the processes were directed mainly to the conversion of the metallic impurities to insoluble salts without any attempt to oxidize the suspending components for the impurities.

50 Suitable coupling agents are found in water miscible oxygenated or nitrogenated organic compounds and particularly in surface active agents. As examples of such components there may be mentioned alcohols such as furfuryl alcohol, secondary butyl alcohol, n-butyl alcohol, isopropyl alcohol; esters such as ethylene glycol monomethyl ether acetate, ethyl acetate; ketones such as cyclohexanone, methyl ethyl ketone, diacetone alcohol; ethers such as diethylene glycol methyl ether; amines such as diethylaminopropylamine. As examples of surface active agents there may be mentioned nonionic surfactants of the ethoxylated nonyl phenol type such as Siponic NP-9 as manufactured by Canadian Alcolac Ltd. or Igepal CO-630 and CO-530 as manufactured by General Aniline & Film Corp., nonionic surfactants of the ethoxylated alcohol types such as Siponic Y500 ethoxylated oleyl alcohol as manufactured by Alcolac Inc. or Renex 30 ethoxylated tridecyl alcohol as manufactured by Atlas Chemical Industries Inc., nonionic surfactants of the sorbitan monolaurate type such as Span 20 as manufactured by Atlas Chemical Industries Inc., nonionic surfactants of alkanolamine condensate type such as Witcamide 5138-A as

manufactured by Witco Chemical Inc., cationic surfactants of the polyethoxylated quaternary ammonium salt type such as Ethoquad C/25 as manufactured by Armac Chemicals Division of Akzona Inc., anionic surfactants of the sodium lauryl ether sulfate type such as Sipon ESY (25% active) as manufactured by Alcolac Inc. The words "Span", "Witcamide" and "Ethoquad" are Registered Trade Marks.

As one method of demonstrating a material's affinity for the used oil we may consider the following. When secondary butanol is blended into a stripped, used automotive lubricating oil at about 3% by weight, a good apparent solution of the alcohol in the oil is obtained, indicating affinity for the oil. Since secondary butanol is also water miscible, it follows that this alcohol would make a satisfactory coupling agent for the oil. When ethylene glycol, which is water miscible, is blended into the stripped oil at a similar level, it does not dissolve but dispersed poorly in droplets which may later separate from the oil. Similarly, low levels of the oil do not appear soluble when mixed into ethylene glycol. Ethylene glycol does not make a satisfactory coupling agent. Some materials such as certain ethoxylated fatty alcohol surfactants which are waxy solids, could be blended with hot oil above the melting point of the solid to be evaluated as above. Other solid materials which cannot readily be melted may be more difficult to evaluate. Surfactants which are supplied in water solutions could not obviously, be evaluated this way as supplied. This type of evaluation should be performed in a dehydrated or stripped version of the oil as it is difficult to interpret the results in an oil containing water.

Many materials which are satisfactory coupling agents are not miscible with a lubricating oil base stock which does not contain additives, but are miscible with a compounded lubricating oil containing the additives and are therefore satisfactory providing they also have affinity for water.

With regard to affinity of the coupling agent for water, materials with a relatively low degree of water miscibility can make satisfactory coupling agents. For example, adequate precipitations of impurities have been obtained using diethylene glycol monobutyl ether acetate, which is soluble in water to the extent of only 6.5% or can itself dissolve 3.7% water at 20°C. Some surface active agents which are basically insoluble in water may themselves be adequate solvents for water or have adequate affinity for water by virtue of the hydrophilic groups in the molecule to be effective. Examples are Igepal CO-530 and Span 20 given in Table I.

The level of coupling agent used can vary between the range of from about 0.1 to about 20% by weight of the used oil being treated. Higher levels could be used in some cases but this would not normally be economical unless the coupling agent was reclaimed by distillation or other means. In practice the coupling agent is preferably used at a level of 0.1 to 5% by weight.

In certain cases, it has been found best to use the coupling agent in the range of 0.3 to 0.5% and the oxidizing agent in the range of 0.5 to 1% by weight.

The temperature at which the process of the present invention can be carried out is not usually critical. It can be carried out at normal ambient temperature but obviously the reaction time will be extended over a long period with resulting poor yield. Accordingly where the rate of productivity and yields become a factor it is preferred to carry out the process of the present invention at elevated temperatures which are lower than the boiling point of water. Obviously higher temperatures could be used if the process is carried out under pressure. As an example of suitable elevated temperatures there may be mentioned a range of from 140 to 200°F.

It is preferred though not essential when exercising the process of the present invention that the used lubricating oil will be subjected to a predistillation step before treatment with the process of the present invention. Better reduction of both metallic and organic contaminants are generally obtained when the oil is stripped at a temperature range of from 550 to 600°F., especially when treating used automotive lubricating oil. On the other hand, when treating used railway diesel lubricating oil, the requirement for stripping is not as critical. As an alternative to full stripping, the used lubricating oil may be submitted to a dehydration step by distillation to about 300°F.

In general, the coupling agent may be mixed directly into the oil or may be blended into the aqueous solution of the oxidizing agent.

The reagent preblend, or the individual components are incorporated into the oil with agitation. Precipitation of the sludge may be accelerated by heating. With the selection of a non-volatile coupling agent or one with a relatively high boiling point, good results are obtained by heating the oil to about 140 - 200°F. The sludge is allowed to settle or can be separated by centrifuging or by filtration using filter aids such as diatomaceous earth or perlite. The oil separated from the sludge can be used as is for some applications such as fuel or can be subjected to other refining steps such as clay contacting, vacuum distillation or hydrogenation treatment to produce a light coloured, purified lubricating oil base stock.

The sludge obtained is inoffensive and generally black, relatively fluid and appears homogeneous when a dehydrated oil is treated but may exhibit clear aqueous, black organic and grey components when the starting oil has a relatively high water content.

5 The sludge produced in this process could find use in road oiling, although attention would have to be paid here to the environmental effect of the high metal content of this component. 5

Other more attractive possible uses would be as an extender for rubber, plastics or asphalt, or in roofing materials such as shingles or felt, or in a cement kiln fuel.

10 It has been found that oil impurities can be absorbed by the clinker when the oil is used as a cement kiln fuel. This use for the sludge could trap the contaminants present and prevent their release to the environment. 10

The sludge could also provide a source for the reclamation of metals contained therein, particularly lead.

15 While it appears, preferable to remove the sludge prior to further treatment, it is possible to treat a used oil in accordance with this invention and carry out further refining steps without separating the sludge from the oil. 15

For example, stripped automotive waste oil can be treated in accordance with the current process and then be subjected to clay contacting without removal of the sludge. The clay and sludge containing the impurities can then be filtered out in a single filtration, using filter aids such as diatomaceous earth, to give a relatively light coloured, purified oil. 20

The present invention will be more readily understood by referring to the following Examples which are given to illustrate the invention rather than limit the scope thereof.

#### *Examples 1 - 14*

25 In each of these Examples, 100 gram samples of used automotive lubricating oil stripped by predistillation to 600°F. were treated with an aqueous solution of the oxidizing agent shown in Column 1 in the amount shown in Column 2 and with the coupling agent shown in Column 3 in the amount shown in Column 4 of Table I. 25

30 In Examples 2-4, 11-14, the coupling agent was dissolved or dispersed in the reagent solution just prior to blending into the oil. 30

In Examples 5-10, the coupling agent was mixed into the oil prior to the addition of the oxidizing agent solution.

35 In all Examples mixing was carried with a spatula at room temperature for about 10 minutes. The containers were then conditioned in a water bath at 180°F for 6 hours followed by standing at room temperature for 18 hours. A sludge deposited at the bottom of each container and the oil layer was carefully decanted and its ash content was determined in accordance with the ASTM Method D482. The ash content is a measure of the level of metallic impurities in the oil. 35

40 As shown in Table I, Examples 2-14 where coupling agents were used, exhibit a much more appreciable reduction in ash content than Example 1, where no coupling agent was used. 40

Examples 2 - 10 show the use of different coupling agents with 25% ammonium persulfate in water as the reagent solution. Examples 11 - 14 show the use of various water soluble oxidizing agents other than ammonium persulfate.

45 In Example 11, the water soluble oxidizing agent is Oxone monopersulfate compound, manufactured by E.I. DuPont de Nemours & Co. This is comprised of two moles of potassium monopersulfate, one mole of potassium hydrogen sulfate, and one mole of potassium sulfate. Potassium monopersulfate is the active component. 45

TABLE I  
Reduction of ash content in 100g. samples of stripped oil

Example	Reagent Solution	Level Used	Coupling Agent	Level Used	Initial Ash Content Of Oil Used	Final Ash Content
1	25% Ammonium Persulfate	4.0g	None	- -	1.27%	0.95%
2	25% Ammonium Persulfate	4.0g.	Siponic NP-9	0.3g.	1.27%	0.01%
3	25% Ammonium Persulfate	4.0g.	Ethoquad C/25	0.5g.	1.27%	0.08%
4	25% Ammonium Persulfate	4.0g.	Sipon ESY	1.0g.	1.42%	0.29%
5	25% Ammonium Persulfate	4.0g.	Igepal CO-530	1.0g.	1.42%	0.01%
6	25% Ammonium Persulfate	4.0g.	Span 20	1.0g.	1.42%	0.13%
7	25% Ammonium Persulfate	4.0g.	Furfuryl Alcohol	3.0g.	1.27%	0.01%
8	25% Ammonium Persulfate	4.0g.	Diacetone Alcohol	3.0g.	1.27%	0.16%
9	25% Ammonium Persulfate	4.0g.	Diethylene glycol methyl ether	3.0g.	1.27%	0.24%
10	25% Ammonium Persulfate	4.0g.	Diethylamino-propylamine	3.0g.	1.42%	0.36%
11	17% Oxone (Potassium Monopersulfate)	6.0g.	Siponic Y500	0.5g.	1.10%	0.12%
12	12% Hydrogen Peroxide	6.0g.	Siponic NP-9	0.4g.	1.10%	0.16%
13	11% Sodium Hypochlorite	10.0g.	Siponic NP-9	0.5g.	1.10%	0.18%
14	10% Succinic Acid Peroxide.	10.0g.	Siponic NP-9	1.0g.	1.42%	0.05%

*Examples 15 - 18*

The same procedure as described in Examples 2-14 was used with the reagents being shown in Table II which also shows the metal contents of the oil layers in parts per million and comparison is made with untreated oil. The metal contents were determined by spectrographic analysis. The last line of Table I indicates the yield in percent of the oil recovered after treatment and is based on the initial volume of stripped oil. Higher yields are obtained with longer heating times.

Example	15	16	17	18	Untreated Stripped Oil
Reagent Solution	25% Ammonium Persulfate	17% Oxone (Potassium Monopersulfate)	12% Hydrogen Peroxide	11% Sodium Hypochlorite	
Level Used	4.0g.	6.0g.	6.0g.	10.0g	
Coupling Agent	Siponic NP-9	Siponic Y 500	Siponic NP-9	Siponic NP-9	
Level Used	0.3g.	0.5g.	0.4g.	0.5g.	
Metal content, ppm					
Pb	23.6	429.0	857.0	776.0	3890.0
Fe	8.0	36.7	214.0	249.0	349.0
Zn	14.2	59.5	72.2	91.5	111.0
Na	1.7	25.9	61.6	123.0	117.0
Cu	0.5	17.2	16.0	9.1	40.5
Al	0.6	1.4	6.9	7.4	33.9
Si	0.7	3.0	2.4	2.3	50.3
Cr	0.8	2.4	7.9	7.4	15.3
Sn	1.4	3.9	7.1	6.0	9.8
Yield	88%	90%	85%	72%	

*Examples 19 - 22*

5 Samples of 50 grams of the decanted oil obtained from Examples 15, 16, 17 and 18 respectively were mixed in beakers with 10 grams of activated clay and heated to 525°F on a hot plate with stirring over a period of 90 minutes. Each sample was allowed to cool to 320°F and was filtered through Whatman No. 5 paper using a 71mm diameter Buchner funnel and a vacuum of approximately 25 inches of mercury. In all cases filtration was completed in about 40 seconds. 5

10 The recovered filtered oil was subjected to ASTM colour tests and the metal content was also determined. Both results are reported in Table III. The ASTM oil colour numbers were determined with a Hellige comparator. It will be noted that light coloured oils of very low metal contents are obtained in each case, particularly in Examples 19, 20 and 21. 10

The words "Whatman" and "Hellige" are Registered Trade Marks.

TABLE III

15		<i>Clay contacting of treated stripped oil</i>				15
	Example	19	20	21	22	
20	Reagent	Ammonium Persulfate	Oxone (Potassium Monopersulfate)	Hydrogen Peroxide	Sodium Hypochlorite	20
25	Coupling Agent	Siponic NP-9	Siponic Y500	Siponic NP-9	Siponic NP-9	25
	ASTM Colour	2½	2½	2½	3	
30	Metal Content, ppm					30
	Pb	0.0	0.0	0.3	88.6	
35	Fe	0.1	0.0	0.0	19.2	35
	Zn	0.2	2.0	2.3	17.0	
40	Na	0.0	0.0	0.0	5.0	40
	Cu	0.0	0.1	0.0	0.5	
45	Al	0.0	0.0	0.0	0.0	45
	Si	0.0	0.2	0.4	0.3	
	Cr	0.1	0.1	0.0	0.2	
50	Sn	0.7	2.8	1.6	1.5	50

55 The examples of Table III were repeated using initial treatments in which the coupling agents were omitted. The decanted oil layers were clay treated as described, cooled to 320°F. and filtered as described. Filtration times in all cases were over 10 minutes. In most cases only a small portion of filtrate was obtained after 10 minutes. The filtrates were dark with ASTM oil colours over 8 in each case. 55

60 This type of blinding of filter paper is an indication of a relatively high level of organic contaminants in the oil. The relative ease with which the clay treated oils of Examples 19, 20, 21 and 22 filtered shows the importance of the coupling agent in accomplishing the removal of organic contaminants along with the metallic impurities. 60

*Example 23*

65 A 100 gram sample of used automotive lubricating oil which had been stripped by predistillation to 600°F. was treated with a solution containing 3.0 grams of water, 1.0 gram 65

of ammonium persulfate and 0.3 grams of Siponic NP-9. The solution was mixed into the oil at room temperature in a beaker using a spatula. The mixture was heated at approximately 180°F. for 2 hours on a hot plate. The sludge was not permitted to settle and was not separated from the oil. After the above period, 20 grams of activated clay was added to the beaker, along with 5 grams of diatomaceous earth filter aid as body feed. The oil was heated to 525°F. over a 90 min. period with stirring. A precoat of diatomaceous earth was deposited on crepe filter paper in a Buchner funnel by filtering a dispersion of the diatomaceous earth in hot, clean oil. The amount of precoat was equivalent to 15 lbs. per 100 square feet of filter area. The treated oil, after cooling to 350°F. and stirring, was filtered through the precoat, using a vacuum of approximately 25 inches of mercury.

#### Example 24

A similar clay treatment and filtration was performed on a sample from the same stripped oil which had not been previously treated with the oxidizing agent/coupling agent combination.

Table IV gives ASTM colours and metal contents of the oils obtained in Examples 23 and 24 and of the untreated, stripped oil. A markedly lower metal content and lighter colour is observed with the oil of Example 23 as compared to that of Example 24.

A recovered yield of approximately 80% was obtained in Example 23. The oil colour obtained in Example 23, while relatively light, is seen to be darker than that of similar Example 19, where the sludge was separated from the oil prior to clay treatment.

The method of Example 23 may find a preference in the re-refining of used railway diesel lubricating oil as opposed to automotive, as the end colour is often not regarded as important with this type of oil.

TABLE IV

*Clay contacting a treated stripped oil containing sludge*

Example	23	24	Untreated Stripped Oil
Reagent	Ammonium Persulfate	None	- -
Coupling Agent	Siponic NP-9	None	- -
ASTM Colour	5	Over 8 (Dark)	Over 8 (Dark)
Metal Content ppm			
Pb	0.6	548.0	3720.0
Fe	0.0	137.0	354.0
Zn	1.6	53.2	122.0
Na	0.6	41.0	105.0
Cu	0.0	4.5	34.9
Al	0.0	3.5	22.4
Si	1.2	3.0	29.7
Cr	0.0	3.9	15.2
Sn	2.7	3.6	7.5



In moving from lab scale to pilot plant scale treatments on stripped oil, certain techniques have been found useful in increasing the rate of settlement of the sludge.

5 In using a coupling agent such as Siponic NP-9, the rate of settlement can be improved if part or all of the coupling agent is first dispersed in the oil in solution in a moderate amount of water, such as 5% or 10% based on the amount of oil being treated, followed by dispersion of the oxidizing agent solution. 5

10 Predispersing a coupling agent such as Siponic NP-9 in solution in a relatively low level of a polar organic solvent, such as 0.5% to 2% of diacetone alcohol, based on the oil level, followed by dispersion of the oxidizing agent solution, appreciably improves the rate of settlement. Alternatively, the polar organic solvent may be blended into the oil singly as a first step, followed by an aqueous solution containing both the oxidizing agent and surfactant with good results. 10

15 Another technique for improving the rate of settlement, one which is relatively well known, involves the use of a hydrocarbon solvent as a diluent to reduce the density and/or viscosity of the oil phase. 15

#### *Example 25*

20 Examples 25 and 26 involve the treatment of pilot plant scale quantities of used lubricating oil. In Example 25, stripped automotive lubricating oil was treated. In Example 26, the treatment was performed on waste automotive oil as collected from service stations, with no prior treatment. 20

25 In Example 25 as given in Table V, 100 Imperial gallons (120 U.S. gallons) of oil which had been stripped by predistillation to 600°F, was placed in a small cone bottomed, insulated tank at ambient temperature. A solution of 3 lbs. of Siponic NP-9 in 70 lbs. of water was added and the oil was mixed for 15 minutes with air blown from a line at the bottom of the tank. A solution of 10 lbs. of ammonium persulfate and 2 lbs. of Siponic NP-9 in 40 lbs. of water was then added. The oil was mixed for 10 min. with air followed by 30 min. with live steam to bring the temperature to 200°F. Mixing was discontinued. After 24 hours, the sludge was drawn off from a valve at the bottom of the tank. This was a black, seemingly homogeneous, medium viscosity liquid. The oil layer was clear and lighter in colour than the sludge, but appears dark when examined in volume. Table V gives the metal content of the treated oil in comparison with that of the untreated stripped oil. 30

In Example 25A, a 200 gram sample of treated oil from Example 25 was mixed with 40 grams of activated clay in a beaker and heated to 550°F. over 90 minutes with stirring. The oil was allowed to cool to 350°F and filtered with a Buchner funnel through Whatman No. 5 paper, using a vacuum of approximately 25 inches of mercury. Properties of the clay treated, filtered oil are given in Table V.

TABLE V

*Treatment of 100 imperial gallons (120 U.S. gallons)  
of stripped oil*

Example	25	25A	Untreated Stripped Oil
Metal Content, ppm			
Pb	27.1	0.0	3890.0
Fe	27.3	0.1	349.0
Zn	5.5	0.7	111.0
Na	0.3	0.0	117.0
Cu	0.4	0.0	40.5
Al	2.0	0.0	33.9
Si	0.2	0.0	50.3
Cr	1.3	0.0	15.3
Sn	3.7	1.7	9.8
ASTM Colour	Over 8 (Dark)	2½	Over 8 (Dark)
Gravity, API at 60°F	- -	32	- -
Viscosity at 100°F	- -	255 SUS	- -

**Example 26**

In Example 26 as given in Table VI, 100 Imperial gallons (120 U.S. gallons) of raw waste automotive service station oil having a water content of 9.8% by weight, was placed in a small cone bottomed, insulated tank at ambient temperature. A solution of 15 lbs. of ammonium persulfate and 5 lbs. of Siponic NP-9 in 50 lbs. of water was added and the oil was mixed for 15 minutes with air followed by 30 minutes with live steam to bring the temperature to 200°F. Mixing was discontinued. After 24 hours, the sludge was drawn off from the bottom valve. The sludge portion consisted of a medium viscosity grey component, a clear fluid aqueous component and a black component. The oil portion was relatively clear and dark. A volume of 80-85 Imperial gallons of oil was recovered. This represents a yield of approximately 90% based on the initial volume of dry oil, i.e. the volume of waste oil reduced by the volume of water present. Properties of the treated oil are given in Table VI in comparison with those of the untreated waste oil. Water contents were determined by distillation in accordance with ASTM Method D95.

The treatment of waste oil as illustrated in Example 26 could produce a low metal content material suitable for use as fuel or for blending into other fuel materials.

In Example 26A, a 200 gram sample of treated oil from Example 26 was mixed with 40

grams of activated clay in a beaker and heated to 550°F. over 90 minutes with stirring. The oil was cooled to 350°F and filtered with a Buchner funnel through Whatman No. 5 paper, using a vacuum of approximately 25 inches of mercury. Properties of the clay treated, filtered oil are given in Table VI.

5 It is seen by comparing Tables V and VI that a cleaner product is obtained when a stripped automotive oil is treated as opposed to raw waste oils, using relatively similar treatments on both. 5

10 Treatment of numerous samples of stripped automotive oil as described has given excellent reproducibility in the properties of the treated oil and in those of the clay treated product. Treatment of various samples of raw waste automotive oil as given very good reproducibility in the level of reduction of metal and water contents of the treated oil. However, variations have shown up with subsequent clay treatments in that differences in filtration rates and colour do occur. Higher levels of coupling agents tend to improve this situation. However, a predistillation step is advantageous in re-refining used automotive oil to a lubricating oil base stock when a clay treating step is included in the process. 15

TABLE VI

*Treatment of 100 imperial gallons (120 U.S. gallons)  
of raw waste oil*

Example	26	26A	Waste Oil
Water Content	0.3%	0.0%	9.8%
Ash Content	0.09%	0.03%	1.33%
ASTM Colour	Over 8 (dark)	3½	Over 8 (dark)
Metal Content, ppm			
Pb	186.0	124.0	6390.0
Fe	100.0	6.6	281.4
Zn	22.1	2.0	117.2
Na	1.4	0.8	94.8
Cu	17.5	0.3	40.0
Al	7.3	1.4	40.2
Si	10.6	0.1	64.3
Cr	7.3	0.1	29.3
Sn	4.1	1.6	7.0

#### WHAT WE CLAIM IS:

1. A process for purifying used lubricating oils which comprises mixing a used lubricating oil with an aqueous solution of a water soluble oxidizing agent capable of supplying active or nascent oxygen and a coupling agent having mutual affinity for both water and the used oil thereby causing the precipitation of a sludge containing the impurities, separating the sludge and recovering the purified oil.

2. A process according to Claim 1, wherein the active oxidizing agent is used in an amount of from about 0.1% to about 10% by weight of the used oil.

3. A process according to Claim 1 or 2, wherein the oxidizing agent is a persulfate.

4. A process according to Claim 3, wherein the oxidizing agent is ammonium, sodium or potassium persulfate.

5. A process according to Claim 3, wherein the oxidizing agent is a monopersulfate.  
6. A process according to Claim 4, wherein the oxidizing agent is potassium monopersulfate.  
7. A process according to Claim 1 or 2, wherein the oxidizing agent is a peroxide.  
5 8. A process according to Claim 7, wherein the oxidizing agent is hydrogen peroxide. 5  
9. A process according to any preceding claim wherein the coupling agent is used in an amount of from about 0.1% to about 20% by weight of the used oil.  
10. A process according to any preceding claim wherein the coupling agent is a water miscible oxygen or nitrogen containing organic compound.  
10 11. A process according to any one of Claims 1 to 9 wherein the coupling agent is a 10  
surface active agent.  
12. A process according to Claim 11, wherein the coupling agent is an ethoxylated surface active agent.  
13. A process according to Claim 12, wherein the coupling agent is an ethoxylated 15  
cationic surfactant. 15  
14. A process according to Claim 12, wherein the coupling agent is an ethoxylated nonionic surfactant.  
15. A process according to Claim 12, wherein the surfactant is an ethoxylated alkyl phenol.  
20 16. A process according to Claim 15, wherein the surfactant is an ethoxylated nonyl 20  
phenol.  
17. A process according to Claim 14, wherein the surfactant is an ethoxylated alcohol.  
18. A process according to Claim 14 wherein the surfactant is an ethoxylated tridecyl alcohol.  
25 19. A process according to Claim 14, wherein the surfactant is an ethoxylated fatty 25  
alcohol.  
20. A process according to Claim 14, wherein the coupling agent is an ethoxylated oleyl alcohol.  
21. A process according to any one of Claims 1 to 9, wherein the coupling agent is a 30  
water miscible ester. 30  
22. A process according to any one of Claims 1 to 9, wherein the coupling agent is a water miscible ketone.  
23. A process according to any one of Claims 1 to 9, wherein the coupling agent is a water miscible ether.  
35 24. A process according to any one of Claims 1 to 9, wherein the coupling agent is a 35  
water miscible amine.  
25. A process according to any one of Claims 1 to 9, wherein the coupling agent is a water miscible alcohol.  
40 26. A process according to Claim 25, wherein the coupling agent is furfuryl alcohol. 40  
27. A process for purifying used lubricating oils substantially as hereinbefore defined.  
28. Lubricating oil whenever purified by a process according to any preceding claim.

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